

ABSTRACT

Based around the idea of searching for sustainable alternatives to fossil sources for manufacturing fuels and chemical products, this doctoral thesis addresses the development of new catalytic processes centered on glycerol valorization, which is the main by-product of biodiesel synthesis. In this sense, the main aim focused on using it as a carbon source to generate nitrogen heterocycles of industrial interest, specifically, to produce 2-methylpiperazine and 2-methylpyrazine.

However, due to the low reactivity of glycerol and the severe reaction conditions necessary to carry out the transformations towards these N-heterocycles, previous detailed research to optimize and understand the selective dehydration process of glycerol to hydroxyacetone (or acetol) was undertaken. Through obtaining this intermediate compound, it has been possible to develop efficient and selective nitrogen heterocycles production processes under reasonably moderate reaction conditions.

In this regard, Cu-Mg-Al hydrotalcite precursors give rise to a family of materials based on Cu-Mg-Al mixed oxides capable, if their composition is adequately optimized, of carrying out the selective dehydration of glycerol to acetol continuously with yields of $\approx 40\%$. In addition, these catalysts are stable for more than 8 hours under operational conditions, showing excellent regeneration capacity and reusability.

In the same way, through the combination of catalytic and characterization studies, the interesting mix of acid-base and redox centers exhibited by these materials has allowed for advancing significantly in the state of the art regarding understanding this glycerol catalytic dehydration reaction. Hence, it has been possible to verify the fundamental role of Cu species and, specifically, Cu(I) species present in the catalysts, in the generation of glyceraldehyde as a critical reaction intermediate for acetol production. Similarly, the acid centers of the catalyst facilitate the first adsorption of glycerol, thus accelerating the reaction.

However, the need to achieve higher acetol productivities from glycerol to stand a chance to succeed in the overall strategy motivated the development and study of a second family of catalysts based on copper oxide supported on different metal oxides (SiO_2 , Al_2O_3 and ZrO_2) combining Lewis acid centers and high Cu exposure. The proper selection and optimization of these materials lead to reaching, with several of them, yields of 60% to acetol with much higher glycerol concentrations in the starting feed.

On the one hand, the CuO/ SiO_2 series of materials present a catalytic behavior highly dependent on the CuO dispersion degree. The high dispersion brings with it an upsurge in the Cu active area, higher acidity and, consequently, a superior catalytic activity, being able to pass, with the same compositions, from practically inert materials to catalysts with increased activity. However, an excess of CuO nanoparticles dispersion generates too much acidity, decreasing the acetol yield. On the other hand, the CuO/ Al_2O_3 catalysts show a high dependence on the acid-base properties of the alumina chosen as support. Specifically, the CuO/ Al_2O_3 -*npw* material appears to expose the proper acidity

necessary to enable glycerol adsorption without forming excessive by-products or impairing liquid product yield.

In the study of CuO/ZrO₂ materials, again, the different acid-base properties exhibited by the catalyst as a function of the zirconia phase employed as support determine the catalytic activity. In this sense, CuO/*m*-ZrO₂ has a lower acid density than CuO/*t*-ZrO₂, which entails carrying out the reaction more selectively. Specifically, the former catalyst is the one that, under the chosen reaction conditions, presents the best performance and productivity to the desired product, being able to carry out the process for a longer time and being possible to reuse it. Furthermore, incorporating the CuO nanoparticles by a deposition-precipitation method through the formation of reversed-phase micelles permits generating more active nanoparticles. Therefore, this catalyst can carry out the reaction even with lower Cu contents.

Once several catalytic systems had been established to produce acetol, the generation of the nitrogen heterocycles of interest from the combination of this molecule with ethylenediamine was investigated. First, the materials based on Pd-nanoparticles supported on simple and mixed metal oxides achieved good yields in synthesizing 2-methylpiperazine from acetol and ethylenediamine. Specifically, the Pd/TiO₂-Al₂O₃ catalyst presents high specific activity when forming 2-methylpiperazine (80% yield). These excellent results could be attributed to the enhanced exposure of unsaturated Pd centers observed in this material, critical for activating the C=N double bond and thus proceeding to the hydrogenation of the intermediate imines, which apparently constitutes the limiting reaction step. Secondly, it has been found that, in the presence of a mainly acid catalyst containing Cu, it is possible to dehydrocyclize acetol with ethylenediamine to 2-methylpyrazine and other alkylpyrazines. In this sense, supports such as ZrO₂ and Al₂O₃ turned out to be the most suitable and stable to carry out the reaction. Specifically, the CuO/Al₂O₃-*npw* catalyst yields 50% to 2-methylpyrazine, reaching values close to 60% when, as happened for the CuO/*m*-ZrO₂ catalyst, the precipitation-deposition method by micelles in reverse phase is used to incorporate the CuO nanoparticles. Finally, a proof of concept of 2-methylpyrazine synthesis starting from glycerol by using a specially designed multi-bed catalytic reactor to perform the two-steps process in one-pot with the same CuO-supported catalyst was assayed, with promising results.

In summary, two new catalytic routes have been established to produce nitrogen heterocycles with glycerol as the main carbon source through its derivative hydroxyacetone. Moreover, as demonstrated in this work, it is even possible to design catalytic processes for N-heterocycles production in which the glycerol is fed directly as starting reagent, opening in this way new perspectives in the field of sustainable valorization of biomass-derived platform chemicals.